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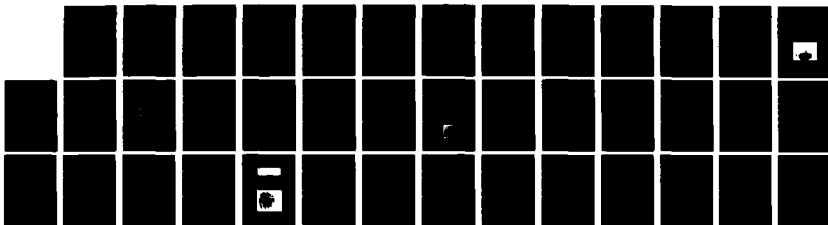
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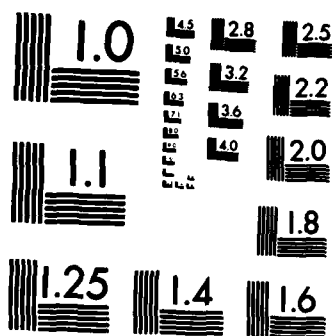
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**STUDY OF MECHANO-CHEMICAL MACHINING  
OF CERAMICS AND THE EFFECT ON  
THIN FILM BEHAVIOR**

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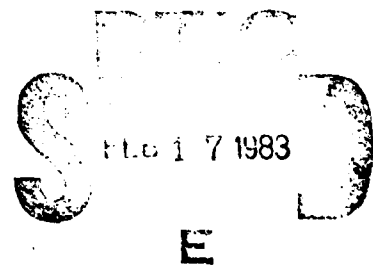
January 1983

Final Technical Report

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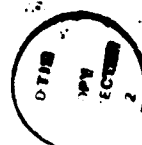
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20. ABSTRACT (CONTINUE ON REVERSE SIDE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER) Efforts have been made in this program to develop mechanochemical polishing technique for a number of materials and to determine the consequences of mechanochemically polished surfaces on the physical performance of ceramics. The objective of the mechanochemical polishing efforts is to produce scratch-and damage-free surfaces by finding suitable soft abrasives that remove material from the workpiece through chemical reactions. Mechanochemical polishing effects were observed when hot-			

pressed and reaction bonded  $\text{Si}_3\text{N}_4$  were polished with two oxides of iron,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . Mechanochemically polished surfaces of  $\text{Si}_3\text{N}_4$  were analyzed using the techniques of Auger electro spectroscopy, profilometry and interferometry. Data showing the effects of mechanochemical polishing on the strenght of hot-pressed  $\text{Si}_3\text{N}_4$  and on the adhesion of thin titanium films on this material have been obtained. Also, preliminary efforts have been made to find suitable soft abrasives for mechanochemical polishing of GaAs, Spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ),  $\text{SiC}$ ,  $\text{B}_4\text{C}$ , and partially stabilized  $\text{ZrO}_2$ .

## Preface

This report and the previous annual technical report cover work performed during the period May 1, 1980 to November 30, 1982 under Office of Naval Research Contract No. N00014-80-C-0437. The authors would like to thank Mr. D.J. Sauve, Jr., for excellent technical support throughout this work, Dr. R. Wagner for evaluating the effects of surface finishing on the adhesion of thin titanium films on hot-pressed  $\text{Si}_3\text{N}_4$ , and Mr. E. Fisher of the Ford Motor Company, Dearborn, Michigan, for providing the fracture strength data on ground and mechanochemically polished hot-pressed  $\text{Si}_3\text{N}_4$ . Auger electron spectroscopy analyses of mechanochemically-polished surfaces were performed by Dr. T. Orent, and RHEED work was performed by Mr. C. Knudson.



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## Table of Contents

Section		Page
1	INTRODUCTION	1
2	RESULTS	3
	2.1 Alumina	3
	2.2 Silicon Nitride	8
	2.2.1 Mechanochemical Polishing	8
	2.2.2 Thin Film Adhesion	14
	2.2.3 Flexural Strength	19
	2.3 Other Materials	22
3	DISCUSSION	25
	INDEX OF PUBLICATIONS	27
	DISTRIBUTION LIST (BASIC)	28
	DISTRIBUTION LIST B (SUPPLEMENTARY)	30

## List of Illustrations

Figure		Page
1	Profile of Ground Surface of Kyocera Sapphire	4
2	RHEED Pattern of Meller Sapphire	4
3	Weight Loss of Kyocera and Meller Sapphire Samples During Dry Mechanochemical Polishing with $\text{SiO}_2$	5
4	Weight Loss of a Polycrystalline Alumina Sample During Dry Mechanochemical Polishing with $\text{SiO}_2$	6
5	Surface Profiles of Coors ADS 995 Alumina (a) Before and (b) After Mechanochemical Polishing	7
6	Weight Loss of Hot-Pressed $\text{Si}_3\text{N}_4$ (Wesgo SNW-1000) During Wet Mechanochemical Polishing with $\text{Fe}_2\text{O}_3$ Under Various Pressures	9
7	Nomarski Micrographs of an $\text{Si}_3\text{N}_4$ Substrate (a) Before and (b) After Mechanochemical Polishing	11
8	Surface Profiles of an $\text{Si}_3\text{N}_4$ Substrate (a) Before and (b) After Mechanochemical Polishing	12
9	Surface Figure of a 2.5 x 2.5 cm $\text{Si}_3\text{N}_4$ Substrate	12
10	Auger Spectra of an $\text{Si}_3\text{N}_4$ Sample Mechanochemically Polished with $\text{Fe}_2\text{O}_3$ . View (a) shows the polished surface and (b) depicts it after sputter-etching.	13
11	Weight Loss During Wet Mechanochemical Polishing with $\text{Fe}_2\text{O}_3$ of a 19mm Diameter Disc of Ceradyne Hot-Pressed $\text{Si}_3\text{N}_4$	15
12	Weight Loss of Reaction Bonded $\text{Si}_3\text{N}_4$ During Wet Mechanochemical Polishing with $\text{Fe}_2\text{O}_3$ . Sample cross-section = 9 x 6.3mm	16
13	Uniaxial Pulltest for Measurement of Thin Film Adhesion	16
14	Auger Profile of the Ti/ $\text{Si}_3\text{N}_4$ Interface. View (a) is hypothetical, assuming no reaction between Ti and $\text{Si}_3\text{N}_4$ . View (b) shows actual profiles.	18
15	$\text{Si}_{2p}$ XPS Peak of Si Single Crystal, $\text{Si}_3\text{N}_4$ and the $\text{Si}_3\text{N}_4/\text{Ti}$ Interface	20



### **List of Illustrations (Concluded)**

<b>Figure</b>		<b>Page</b>
<b>16</b>	<b>Weibull Plot of Standard Test Bars of Hot-Pressed <math>\text{Si}_3\text{N}_4</math></b>	<b>21</b>
<b>17</b>	<b>Weibull Plot of Mechanochemically Polished Bars of Hot-Pressed <math>\text{Si}_3\text{N}_4</math></b>	<b>21</b>
<b>18</b>	<b>Optical Micrograph and Electron Channeling Pattern of Mechanochemically Polished GaAs</b>	<b>23</b>

## **List of Tables**

<b>Table</b>		<b>Page</b>
<b>1</b>	<b>Pulltest Results of Ti Metallization on <math>\text{Si}_3\text{N}_4</math> Substrate</b>	<b>17</b>
<b>2</b>	<b>Fracture Strengths of Standard and Mechanochemically Polished Test Bars of Hot-Pressed <math>\text{Si}_3\text{N}_4</math></b>	<b>20</b>
<b>3</b>	<b>Potential Soft Abrasives for Mechanochemical Polishing of Various Materials</b>	<b>24</b>

## Section 1

### Introduction

Efforts have been made in this program to develop mechanochemical polishing techniques for a number of materials. In this technique, a hard brittle material (mostly ceramics and some semiconductors, such as silicon) is polished with suitable abrasive whose hardness is less than that of the workpiece. Since such an abrasive cannot damage or scratch the workpiece, the technique can yield damage- and scratch-free surfaces. Even though the abrasive used in mechanochemical polishing is soft, the observed rate of material removal is often high and comparable to that achieved with harder abrasives. One proposed explanation is that chemical reactions occur at the contact points between the abrasive and the workpiece.<sup>1</sup> These transformed regions, which are believed to be very small (of the order of 100 Å), then detach themselves from the workpiece during polishing.

Mechanochemical polishing is performed in a manner very similar to conventional polishing (using conventional polishing machines). However, in order to promote the chemical reaction, it is often necessary to generate high temperatures at the contact points between the abrasive and the workpiece. A simple way to accomplish this is to apply pressure in the order of  $7 \times 10^4 \text{ N/m}^2$  (10 psi) on the workpiece and to perform the mechanochemical polishing "dry." In some cases, chemical reactions can be induced at moderate temperatures and significant removal rates are observed, even when the mechanochemical polishing is performed "wet." The terms dry and wet refer to the use of a loose powder of soft abrasive as the polishing medium in the former case and a slurry of a soft abrasive in a liquid (usually water) as the polishing medium in the latter case.

In connection with wet and dry mechanochemical polishing, it should be noted that the chemical reactions involved in surface finishing can be broadly classified into two types: (1) solid-solid and (2) solid-liquid. Dry mechanochemical polishing of silicon with soft abrasives such as  $\text{CaCO}_3$ ,  $\text{BaCO}_3$  and  $\text{MgO}$  is an example of mechanochemical polishing involving solid-solid type of chemical reaction. Each of these abrasives yields highly reflecting silicon surfaces showing few scratches. Such surfaces are also obtained when silicon is polished with a slurry of any of these abrasives in water. The observed material removal in this case can be due to both solid-solid and solid-liquid type of chemical reactions if, for example, the slurry dissolves silicon at temperatures generated by the rubbing of silicon surfaces against the surfaces of the abrasive and the lap.

---

<sup>1</sup>N. Yasunaga, N. Tarumi, A. Obara and O. Imanaka, in *The Science of Ceramic Machining and Surface Finishing II*, B.J. Hockey and R.W. Rice, editors. National Bureau of Standards Special Publication 562, 1979, 171.

Slurries of many soft abrasives in water are not neutral. Since some materials dissolve in acidic or basic solution, at or slightly above room temperature, liquid-solid type of chemical reactions can make significant contribution to the removal rates observed during wet mechanochemical polishing. An adjustment of the pH of the slurry provides an important means for controlling removal rates in such cases.

The emphasis of most of our efforts in this program have been on determining the feasibility of surface finishing of a number of materials through solid-solid type of chemical reactions. Typically, these efforts involve polishing a given material containing dull surface, such as that produced by grinding or lapping with hard and coarse abrasives, in dry condition with a number of soft abrasives using pressures of the order of  $3.5 \times 10^3$  to  $7 \times 10^3$  N/m<sup>2</sup> (5-10 psi). If an abrasive reacts chemically with the workpiece, it will produce scratch-free and highly reflecting surfaces. In many cases, such as polishing of alumina with SiO<sub>2</sub> particles or of silicon nitride with Fe<sub>2</sub>O<sub>3</sub>, no significant changes in the removal rates occur when the polishing mode is changed from dry to wet. The latter is the preferred mode of mechanochemical polishing because it minimizes chipping at the edges of the sample, results in quieter polishing operation, and makes it easier to control the flatness of the sample.

Some of our observations concerning the mechanochemical polishing effects in the case of silicon and alumina were reported in the previous report.<sup>2</sup> In this report, we are reporting the results of our efforts to develop mechanochemical polishing techniques for Si<sub>3</sub>N<sub>4</sub>, evaluate the effect of mechanochemical polishing on the strength and the thin film adhesion in the case of Si<sub>3</sub>N<sub>4</sub>. Also described are our preliminary observations of mechanochemical polishing effects in the case of GaAs, zirconia, SiC, B<sub>4</sub>C and spinel (MgO · Al<sub>2</sub>O<sub>3</sub>).

---

<sup>2</sup>H. Vora and R.J. Stokes, Office of Naval Research Annual Technical Report No. NOOC14-80-C-0437-1, (1981).

## Section 2

### Results

#### 2.1 ALUMINA

There are many factors that contribute to the removal rates obtained in mechanochemical polishing. Among these are the roughness of the sample and the damaged layer introduced by previous grinding or lapping operations. To illustrate the effects of these factors, removal rates obtained by dry mechanochemically polishing three different types of alumina with  $\text{SiO}_2$  particles were measured. Two of these were single-crystal alumina of  $(10\bar{1}0)$  orientation, one purchased from Kyocera and the other from Adolf Meller Co. The third was polycrystalline alumina (COORS ADS 995). Kyocera sapphire contained a thick damaged layer introduced by previous grinding operation; its surface profile is shown in Figure 1. The surface of Meller sapphire was scratch-free and also appeared to be damage-free, as shown by its RHEED pattern in Figure 2.

All alumina samples were  $2.5 \times 2.5$  cm in cross-section and were dry mechanochemically polished on a 25 cm diameter linen bakelite lap, using a submicron size  $\text{SiO}_2^*$  as abrasive. The experiments were conducted on a Strasbaugh polishing machine, model 6Y-1, using a lap rpm of 50 and a stroke frequency of 20 cpm.

Data on the amount of material removed as a function of polishing time for Kyocera and Meller sapphire samples are shown in Figure 3. These data indicate that in the case of Kyocera sapphire, which contained a thick damaged layer with a very rough surface, the removal rate is high in the beginning but decreases rapidly, with polishing time, from the average value of  $\sim 2\mu\text{m/hr}$  for the first hour of polishing to a steady value of  $\sim 0.4\mu\text{m/hr}$ , reached after about 5 hours of polishing at a pressure of  $7 \times 10^4 \text{ N/m}^2$  (10 psi). Whereas in the case of Meller sapphire, which contained few scratches and a thin or no damaged layer, the removal rate at a given pressure does not change with polishing time and increases with increasing pressure from a value of  $\sim 0.3\mu\text{m/hr}$  at  $3.5 \times 10^4 \text{ N/m}^2$  (5 psi) to  $\sim 0.6\mu\text{m/hr}$  at  $1.4 \times 10^5 \text{ N/m}^2$  (20 psi).

Observations made in the case of polycrystalline alumina (COORS ADS 995) were similar to those made in the case of Kyocera sapphire, although the steady material removal rate was slightly higher in the latter case,  $\sim 0.34\mu\text{m/hr}$  for polycrystalline  $\text{Al}_2\text{O}_3$ , as compared to  $\sim 0.4\mu\text{m/hr}$  for Kyocera sapphire at a pressure of  $7 \times 10^4 \text{ N/m}^2$  (10 psi). The weight loss data of COORS ADS 995 alumina are shown in Figure 4, and its surface profiles, measured before and after mechanochemical polishing with  $\text{SiO}_2$ , are shown in Figure 5. It can be seen that mechanochemical polishing reduces the peak-to-valley roughness of COORS ADS 995 aluminum from  $\sim 6000\text{\AA}$  to  $\sim 300\text{\AA}$ .

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\*Cerac Incorporated, Milwaukee, Wisconsin

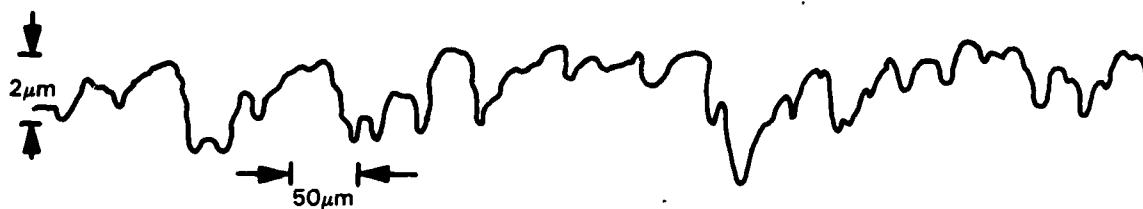


Figure 1. Profile of Ground Surface of Kyocera Sapphire

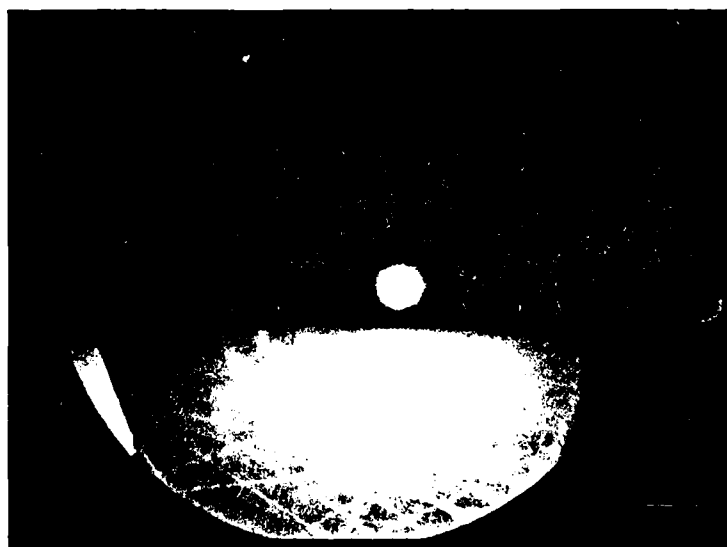


Figure 2. RHEED Pattern of Meller Sapphire

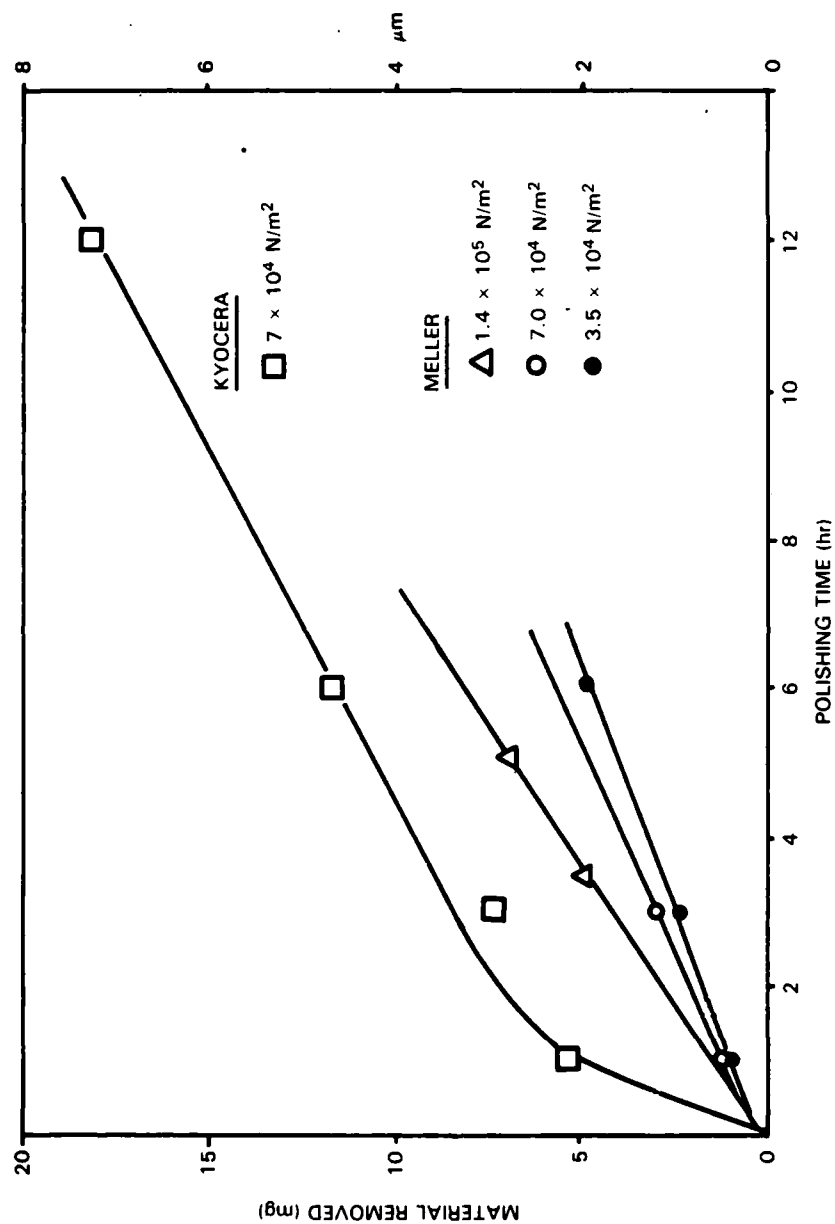


Figure 3. Weight Loss of Kyocera and Meller Sapphire Samples During Dry Mechanochemical Polishing with  $\text{SiO}_2$

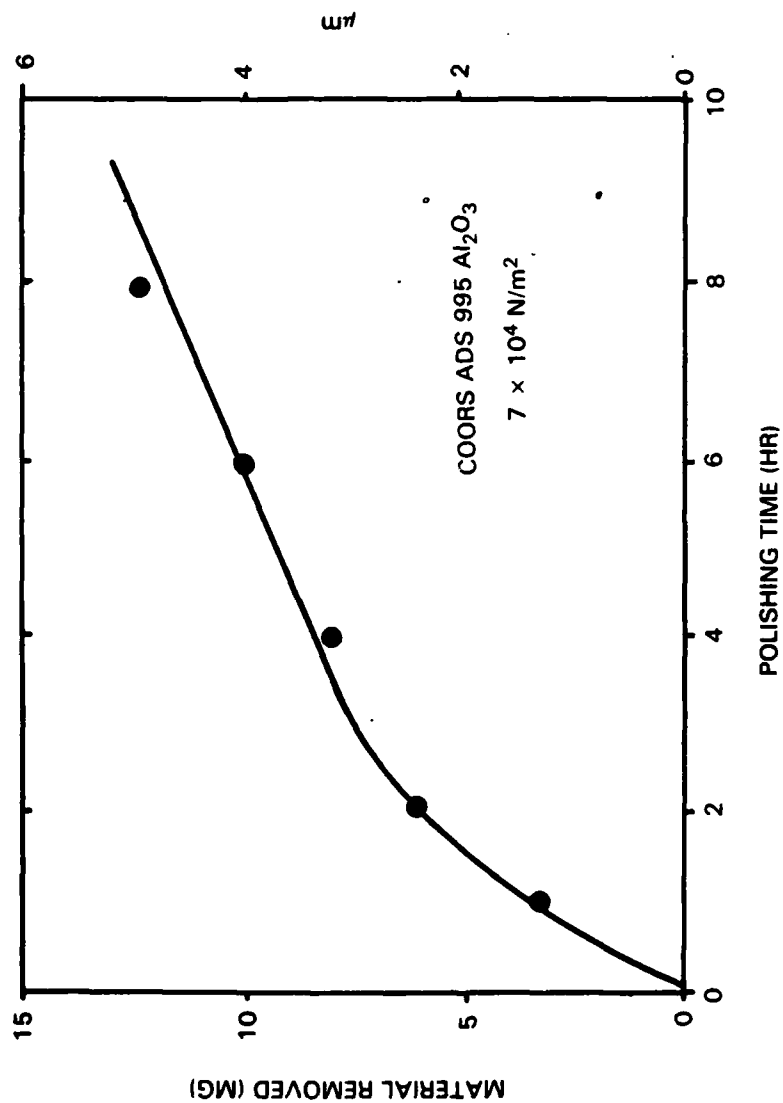


Figure 4. Weight Loss of a Polycrystalline Alumina Sample During Dry Mechanochemical Polishing with  $\text{SiO}_2$



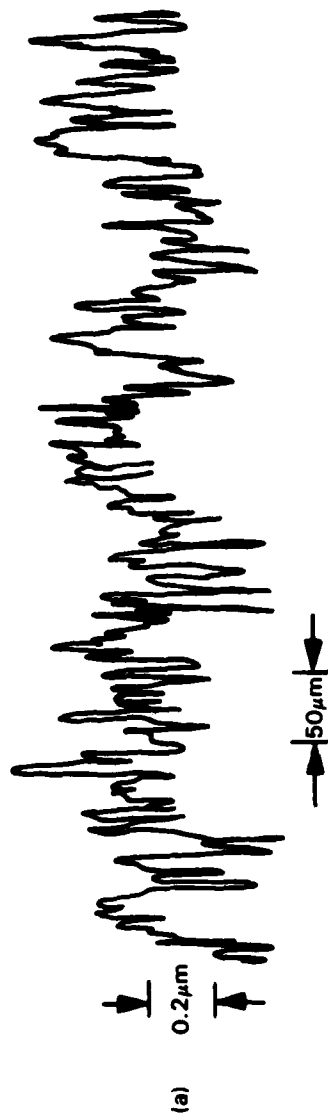


Figure 5. Surface Profiles of Coors ADS 995 Alumina (a) Before and (b) After Mechanical Polishing

## 2.2 SILICON NITRIDE

### 2.2.1 Mechanochemical Polishing

Our initial efforts to develop a mechanochemical polishing technique for silicon nitride were made using Wesgo SNW-1000 hot-pressed  $\text{Si}_3\text{N}_4$ .<sup>\*</sup> It contained 87 w/o  $\text{Si}_3\text{N}_4$ , and 11 w/o  $\text{Al}_2\text{O}_3$  and 2 w/o  $\text{Y}_2\text{O}_3$  for densification. It was purchased in the form of substrates of approximate dimensions of  $2.5 \times 2.5 \times 0.1$  cm. Three substrates were mounted on a 10 cm diameter sample holder and attempts were made to mechanochemically polish them using several soft abrasives,  $\text{CaCO}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ , on a 25 cm diameter linen bakelite lap rotated at speeds up to 50 rpm. These experiments were conducted using a Strasbaugh polishing machine (model 6Y-1) and loads of up to 10 kgs were applied to the sample holder. Under these experimental conditions, scratch-free surfaces were readily obtained when  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  was used as the soft abrasive. Consequently, the efforts were concentrated on these two abrasives. The  $\text{Fe}_2\text{O}_3$ <sup>\*\*</sup> particle size was  $3\mu\text{m}$  or less, and the  $\text{Fe}_3\text{O}_4$ <sup>†</sup> was  $5\mu\text{m}$  or less.

Data on the amount of material removed as function of polishing time during wet mechanochemical polishing with  $\text{Fe}_2\text{O}_3$  are shown in Figure 6 for three different pressures. For these experiments, a single substrate was mounted at the center of the holder and mechanochemically polished on a 25 cm diameter linen bakelite lap, rotating at 20 rpm until it was scratch-free. The sample was then removed from the holder, and its weight was measured. The subsequent decrease in weight, with a polishing time, for pressures of  $0.7 \times 10^4 \text{ N/m}^2$  (1 psi),  $3.5 \times 10^4 \text{ N/m}^2$  (5 psi) and  $7.0 \times 10^4 \text{ N/m}^2$  (10 psi) are shown in Figure 6. Increasing the pressure from  $0.7 \times 10^4 \text{ N/m}^2$  (1 psi) to  $3.5 \times 10^4 \text{ N/m}^2$  (5 psi) increased the removal rate by more than a factor of 10, but further increase in pressure had no significant effect on the removal rate, i.e., the removal rate reached a saturation value of  $\sim 1.6\mu\text{m/hr}$  at a pressure of  $3.5 \times 10^4 \text{ N/m}^2$  (5 psi). In an effort to determine whether the removal rate can be increased further, the  $\text{Si}_3\text{N}_4$  substrate was dry mechanochemically polished, using a pressure of  $7 \times 10^4 \text{ N/m}^2$  (10 psi). This did not increase the removal rate; the measured removal rate under this condition was  $\sim 1.5\mu\text{m/hr}$ .

---

<sup>\*</sup>Wesgo Division, GTE Products Corporation, Belmont, California

<sup>\*\*</sup>Buehler Ltd., Lake Bluff, Illinois

<sup>†</sup>Cerac Incorporated, Milwaukee, Wisconsin

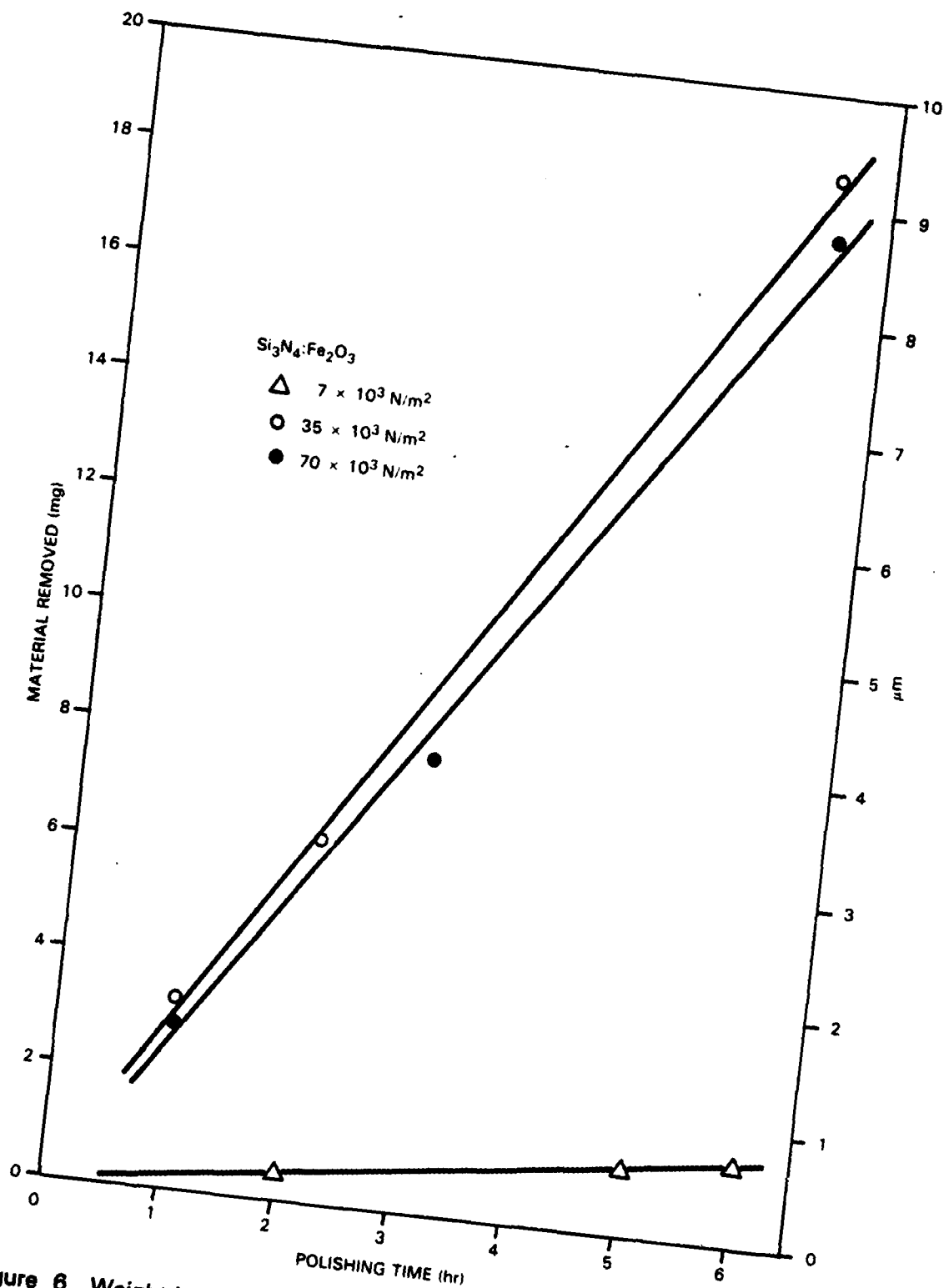


Figure 6. Weight Loss of Hot-Pressed Si<sub>3</sub>N<sub>4</sub> (Wesgo SNW-1000) During Wet Mechanochemical Polishing with Fe<sub>2</sub>O<sub>3</sub> Under Various Pressures

Mechanochemically polished  $\text{Si}_3\text{N}_4$  samples were subjected to visual and optical microscopic examinations and, in addition, their surface roughness was measured using a Talystep profilometer.\* In these tests, both  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  polished surfaces appeared to be of comparable quality.

The visual examination indicated that the mechanochemically polished  $\text{Si}_3\text{N}_4$  samples had mirror finishes and much higher reflectivities than as-received samples polished conventionally by Wesgo with hard abrasives. The optical microscopic examination of the entire polished surface did not reveal any scratches. Figure 7 compares the Nomarski micrographs of an  $\text{Si}_3\text{N}_4$  substrate before (in the as-received condition) and after mechanochemical polishing with  $\text{Fe}_2\text{O}_3$ . The corresponding surface profiles are shown in Figure 8, where it is seen that mechanochemical polishing reduced the peak-to-valley roughness of  $\text{Si}_3\text{N}_4$  by a factor of 5 to a value of  $\sim 200\text{\AA}$ . The hot-pressed  $\text{Si}_3\text{N}_4$  substrates used in this work were polycrystalline. Thus, the ultimate smoothness that could be achieved by mechanochemical polishing was limited by the grain boundaries, second phases and pores present in the material.

Because of the high reflectivity, it was possible to determine the flatness of mechanochemically polished  $\text{Si}_3\text{N}_4$  substrates, using an interferometric technique. The surface figure of a  $2.5 \times 2.5$  cm  $\text{Si}_3\text{N}_4$  substrate is shown in Figure 9. This figure was obtained using a HeNe laser as a light source ( $\lambda = 633$  nm) and indicates a flatness of  $\sim 3$  wave.

The surface of an  $\text{Si}_3\text{N}_4$  substrate that had been mechanochemically polished with  $\text{Fe}_2\text{O}_3$  and rinsed in acetone was analyzed by Auger electron spectroscopy (AES) using a scanning Auger microscope (3 keV,  $1\mu\text{A}$ ). The surface spectrum shown in Figure 10(A) indicated that the major contaminants were oxygen and carbon. Repeated scans across the region containing the strongest iron peak did detect approximately 0.5 atomic percent iron in the surface layer. The peak positions and fine structure observed in high-resolution scans of the Si (LVV), N (KLL) and O (KLL) Auger peaks closely resembled those of an oxygen-rich silicon oxynitride.<sup>3</sup> The sample was sputter-etched with 4 keV argon ions until carbon was no longer detectable [Figure 10(B)]. The roughness of the surface [see Figure 8(b)] made an accurate determination of the sputter depth impossible, but it was estimated that no more than  $100\text{\AA}$  had been removed. No Fe was detected after sputter etching, but traces of Y and Al, which are constituents of the bulk material, were seen. The oxygen level had been reduced by a factor of five, and the Si (LVV) and N (KLL) peaks had the characteristic energies and shapes of sputtered  $\text{Si}_3\text{N}_4$ .<sup>3-5</sup>

\*Rank Taylor Hobson, Leicester, England

3R. Hezel and N. Liske, "Si (LVV) Auger Spectra of Amorphous Si-Oxide, Si-Nitride, and Si-Oxynitride," J. Appl. Phys. 51 (5) 2566-2568 (1980).

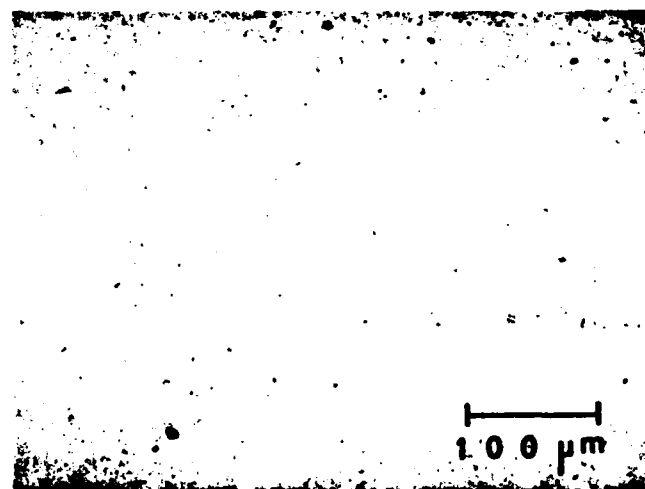
4S. Thomas and R.J. Mattox, "An Attempt at the AES Evaluation of the Composition of Off-Stoichiometric Silicon Nitride," J. Electrochem. Soc. 124 (12) 1942-1945 (1977).

5P.H. Holloway, "Chemical Shifts in Auger Electron Spectra from Silicon in Silicon Nitride," Surface Science 54 (2) 506-508 (1976).

(a)



(b)



**Figure 7. Nomarski Micrographs of an  $\text{Si}_3\text{N}_4$  Substrates (a) Before and (b) After Mechanochemical Polishing**

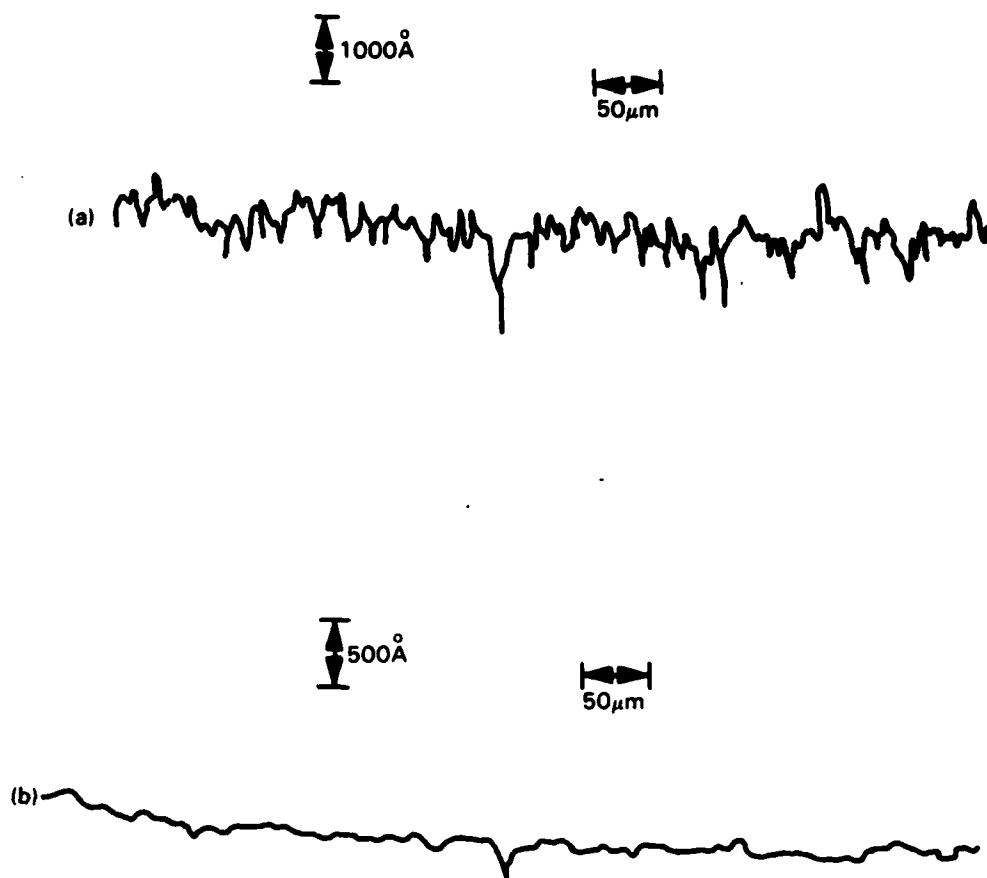


Figure 8. Surface Profiles of an  $\text{Si}_3\text{N}_4$  Substrates (a) Before and (b) After Mechanochemical Polishing

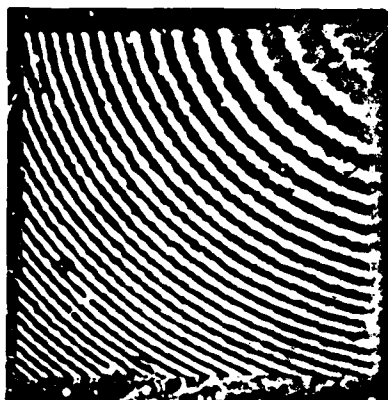


Figure 9. Surface Figure of a 2.5 X 2.5 cm  $\text{Si}_3\text{N}_4$  Substrate

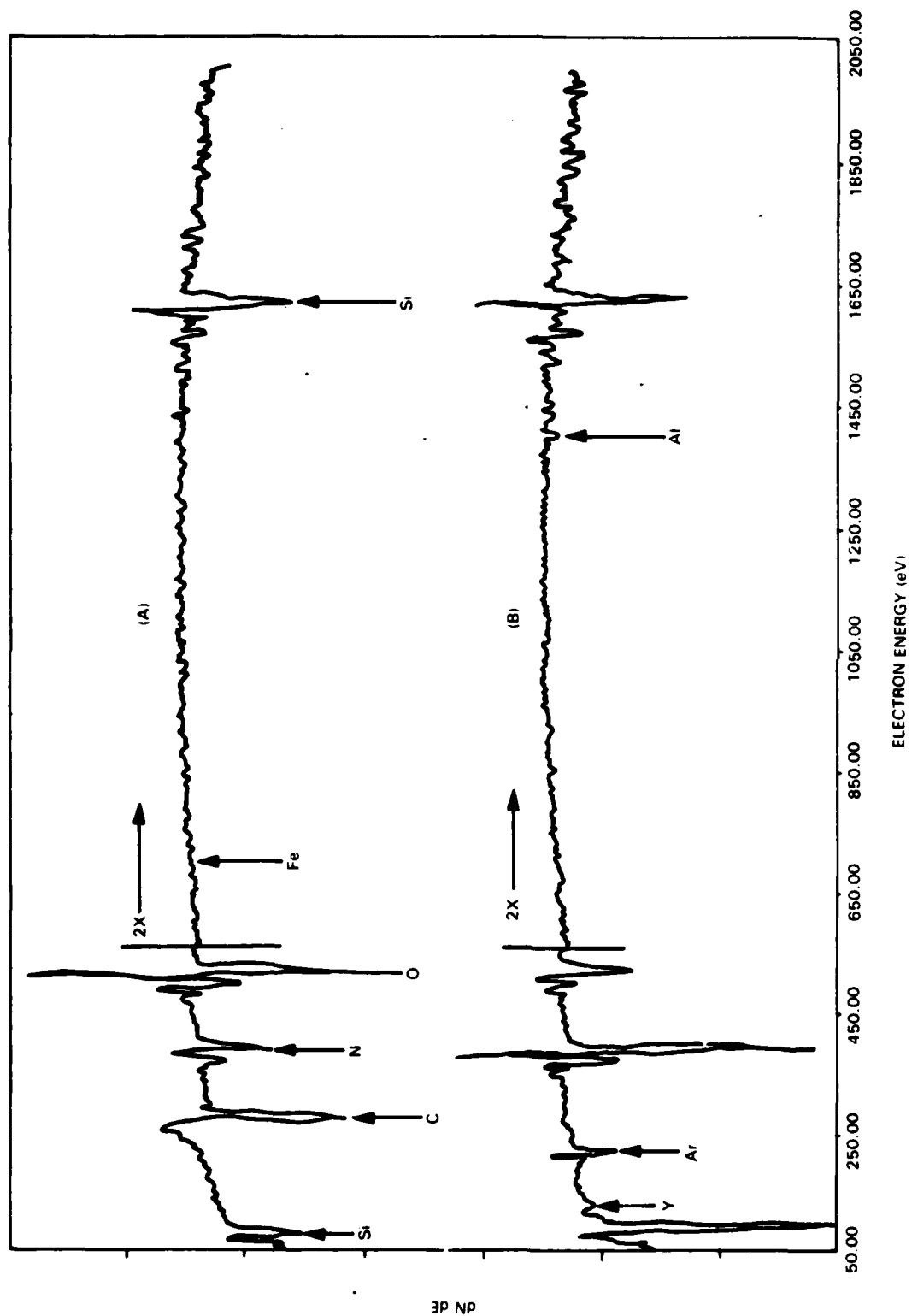


Figure 10. Auger Spectra of an  $\text{Si}_3\text{N}_4$  Sample Mechanochemically Polished with  $\text{Fe}_2\text{O}_3$ . View (a) shows the polished surface and (b) depicts it after sputter-etching.

During the course of this work, hot-pressed  $\text{Si}_3\text{N}_4$  samples manufactured by Norton (NC-132), Demetron, and Ceradyne, and a few samples of reaction-bonded  $\text{Si}_3\text{N}_4$ , were also mechanochemically polished with  $\text{Fe}_2\text{O}_3$ . Norton and Ceradyne hot-pressed  $\text{Si}_3\text{N}_4$  and the reaction-bonded  $\text{Si}_3\text{N}_4$  were observed to mechanochemically polish at significantly higher rates than Wesgo or Demetron  $\text{Si}_3\text{N}_4$ . The measurements were made of the removal rates achieved by wet mechanochemical polishing with  $\text{Fe}_2\text{O}_3$  of Ceradyne  $\text{Si}_3\text{N}_4$  and reaction-bonded  $\text{Si}_3\text{N}_4$ , using the same procedure described earlier for Wesgo  $\text{Si}_3\text{N}_4$ . Weight loss data for Ceradyne and reaction-bonded  $\text{Si}_3\text{N}_4$  are shown in Figures 11 and 12, respectively. Note that the measured removal rate at a pressure of  $7 \times 10^4 \text{ N/m}^2$  (10 psi) for Ceradyne  $\text{Si}_3\text{N}_4$  is about a factor of 2.5 higher, and at a pressure of  $2.8 \times 10^5 \text{ N/m}^2$  (40 psi) for reaction-bonded  $\text{Si}_3\text{N}_4$  is about a factor of 4 higher, than the maximum removal rate of  $\sim 1.6 \mu\text{m/hr}$  measured for Wesgo SNW-1000  $\text{Si}_3\text{N}_4$  (Figure 6). The reasons for these variations are not understood at this time.

### 2.2.2 Thin Film Adhesion

Integrated circuit electronics packaging for future systems with increased circuit densities will need decreasing substrate feature sizes and larger chip dimensions. In order to minimize reliability problems, the substrate should contain minimum defects (such as scratches, pores, pits and pullouts) and its roughness should be much smaller than the width of the metallization lines. Employment of a soft abrasive in mechanochemical polishing yields scratch-free surfaces containing minimum extrinsic defects and, in this respect, mechanochemically polished surfaces are expected to perform better in electronics packaging than the surfaces polished conventionally with hard abrasives. However, the maximum surface smoothness that can be permitted in electronics packaging is also limited by the adhesion of the metal films to the substrate. This is because the adhesion of metal films to a ceramic substrate is mainly due to two factors: (1) mechanical keying, or interlocking, into irregularities of the substrate surface, and (2) chemical bonding. The contribution of the mechanical keying to thin film adhesion decreases with the decreasing surface roughness of the sample, and this can lead to poor thin film adhesion in the case of smooth surfaces.

Measurements of the adhesion of titanium metallization ( $\sim 1000\text{\AA}$  thick) to the rough and smooth surfaces of hot-pressed  $\text{Si}_3\text{N}_4$  have been made.  $\text{Si}_3\text{N}_4$  was selected because it is a potential substrate material for future generations of integrated circuits.  $\text{Si}_3\text{N}_4$  can be made by hot-pressing, as well as by tape casting, with thermal conductivity comparable to that of alumina and with a coefficient of thermal expansion that matches that of silicon.

Adhesion of Ti metallization to  $\text{Si}_3\text{N}_4$  was determined using a uniaxial tension pull test. As shown in Figure 13, a presoldered wedge-shaped brass stud is attached to a presoldered square on the substrate. For connecting the stud and the metallized substrate, silver solder (95 w/o Sn, 5 w/o Ag) was used. The bonded stud was pulled



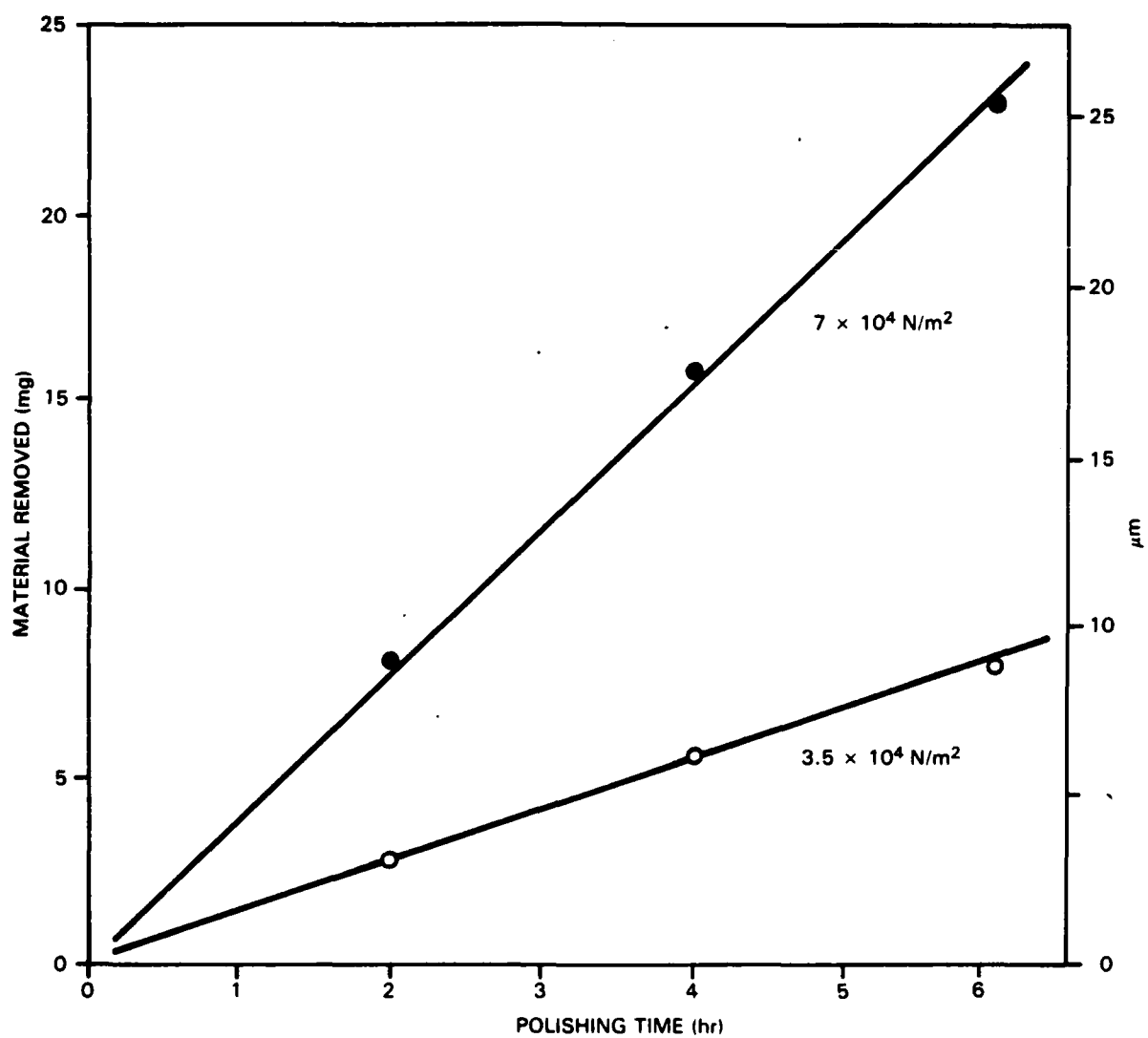


Figure 11. Weight Loss During Wet Mechanochemical Polishing with  $\text{Fe}_2\text{O}_3$  of a 19mm Diameter Disc of Ceradyne Hot-Pressed  $\text{Si}_3\text{N}_4$

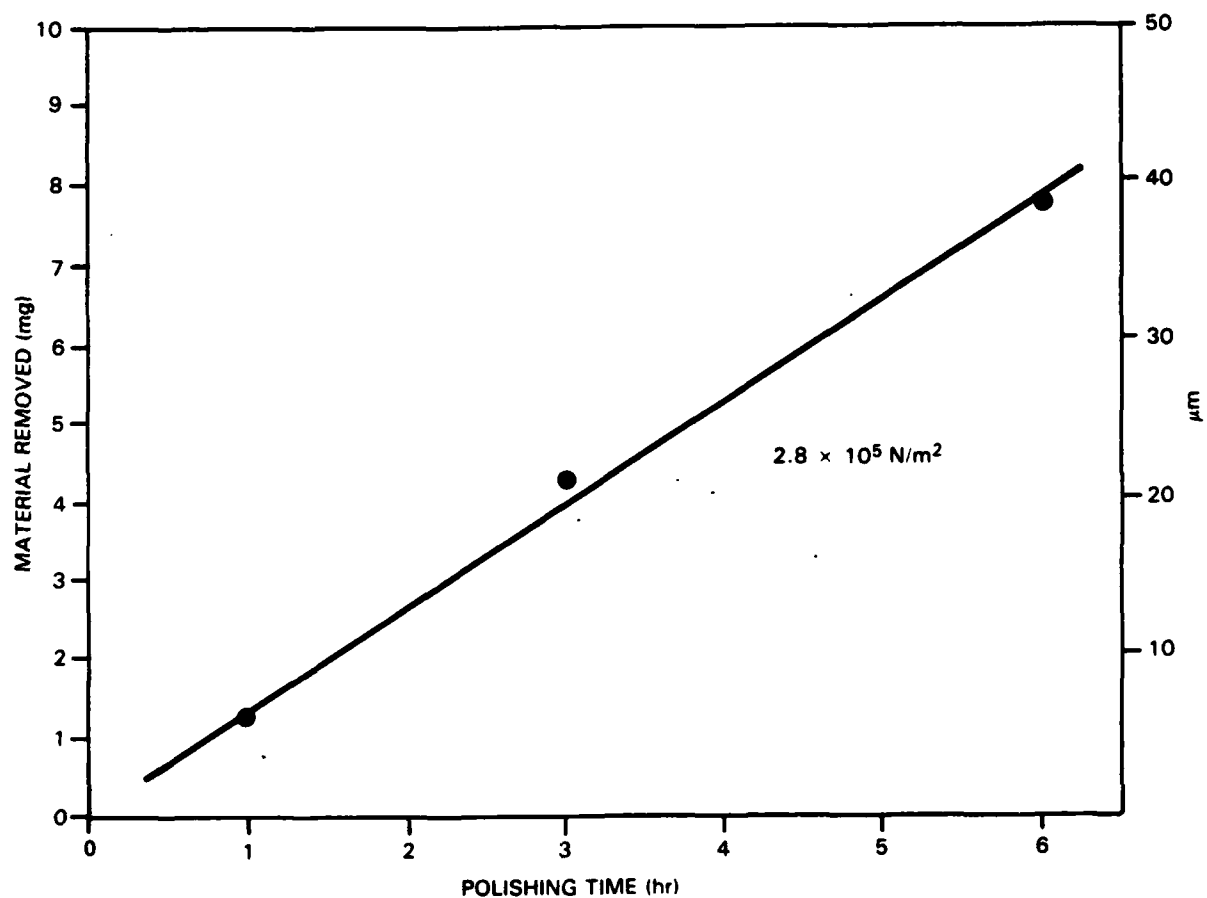


Figure 12. Weight Loss of Reaction-Bonded  $\text{Si}_3\text{N}_4$  During Wet Mechanochemical Polishing with  $\text{Fe}_2\text{O}_3$ . Sample cross-section =  $9 \times 6.3\text{mm}$ .

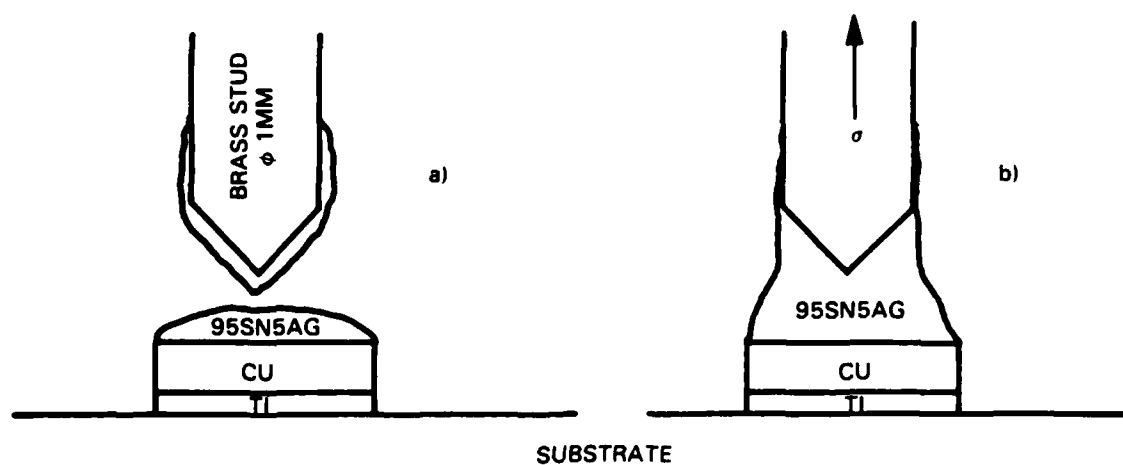


Figure 13. Uniaxial Pulltest for Measurement of Thin Film Adhesion

in an Instron testing machine, using a crosshead speed of 0.13 cm/mnt. In this test, the failures in most cases were observed to occur at the substrate/metallization interface. Square pads of two different sizes,  $500 \times 500 \mu\text{m}$  and  $1250 \times 1250 \mu\text{m}$ , were used. Wesgo SNW-100  $\text{Si}_3\text{N}_4$  was used as the substrate and the adhesion measurements were made both before and after mechanochemical polishing. Mechanochemical polishing reduced the surface roughness by about a factor of five to a peak-to-valley value of  $\sim 200\text{\AA}$ , as noted earlier in Figure 8.

The results of pull test measurements of Ti- $\text{Si}_3\text{N}_4$  metallizations are summarized in Table 1, where it is noted that the reduction in the surface roughness of  $\text{Si}_3\text{N}_4$  by mechanochemical polishing reduces thin film adhesion. The fact that adhesion occurs even on smooth surfaces produced by mechanochemical polishing indicates that some chemical bonding occurs between Ti and  $\text{Si}_3\text{N}_4$ . To verify this, a  $200\text{\AA}$  thick layer of Ti was RF sputter deposited on the mechanochemically polished surface of Wesgo SNW-100  $\text{Si}_3\text{N}_4$ . The Ti- $\text{Si}_3\text{N}_4$  interface was then analyzed using both Auger electron spectroscopy and X-ray photoelectron spectroscopy (XPS).

Figure 14(a) shows a hypothetical Auger profile that would be expected from Ti- $\text{Si}_3\text{N}_4$  system if no reaction occurred at the interface. Sputtering through the Ti layer revealed distribution profiles for various elements which were significantly different. The actual profiles are shown in Figure 14(b), where it is noted that Ti can be detected well below the original Ti- $\text{Si}_3\text{N}_4$  interface and that the Si concentration in the interface region is lower compared to that in the bulk  $\text{Si}_3\text{N}_4$ . These data indicate that there is a diffusion of Ti into a thin ( $\sim 200\text{\AA}$ ) surface layer of  $\text{Si}_3\text{N}_4$ .

Table 1. Pulltest Results of Ti Metallization on  $\text{Si}_3\text{N}_4$  Substrate

Substrate Condition	Failure Load, kg	
	$500 \mu\text{m} \times 500 \mu\text{m}$ Pad	$1250 \mu\text{m} \times 1250 \mu\text{m}$ Pad
As received	$1.4 \pm 0.5$	$5.6 \pm 1.8$
Mechanochemically polished	$0.9 \pm 0.5$	$3.6 \pm 1.4$

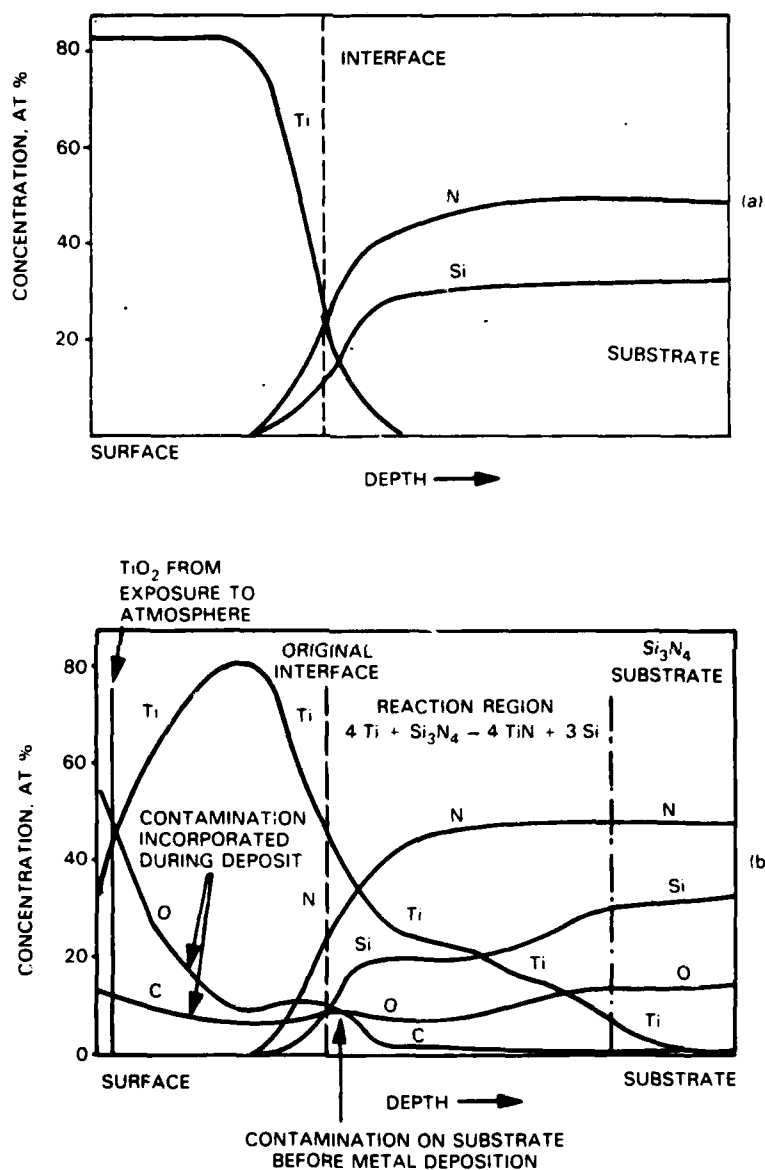


Figure 14. Auger Profile of the Ti/Si<sub>3</sub>N<sub>4</sub> Interface. View (a) is hypothetical, assuming no reaction between Ti and Si<sub>3</sub>N<sub>4</sub>. View (b) shows actual profiles.

XPS analysis indicated that different elements have reacted with each other. Figure 15(a) shows  $\text{Si}_{2p}$  XPS peak of pure silicon sample and Figure 15(c) shows that of  $\text{Si}_3\text{N}_4$ . XPS spectrum of the reaction region revealed the presence of both these peaks, as shown in Figure 15(b), thereby indicating the likelihood of the occurrence of the reaction  $4\text{Ti} + \text{Si}_3\text{N}_4 \rightarrow 4\text{TiN} + 3\text{Si}$ . Further evidence of TiN formation was obtained by monitoring  $\text{Ti}_{2p}$  XPS peak. XPS spectrum obtained from within the reaction region indicated the presence of two peaks, one originating from pure Ti and the other from TiN.

Figure 14(b) also shows the concentration profiles of O and C. The increasing concentration of these two elements towards the surface is due to contamination during the deposition. The relatively high C concentration at the original interface is probably due to cleaning the substrate with acetone before sputter deposition of the metallization. The high oxygen level within the substrate is due to the presence of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , which are used as densification aids for  $\text{Si}_3\text{N}_4$ .

### 2.2.3 Flexural Strength

Hot pressed  $\text{Si}_3\text{N}_4$  is an important candidate material for ceramic heat engine parts. For this reason efforts were made in this program to determine the effect of mechanochemical polishing on the strength of hot-pressed  $\text{Si}_3\text{N}_4$ .

Four-point-bend specimens, ~25cm long, were cut from a billet of Norton NC-132  $\text{Si}_3\text{N}_4$  such that both the fracture surface and the fracture propagation direction would be parallel to the hot-pressing direction. The specimens were then ground to a final cross-section of  $3.2 \times 1.6$  mm, using a 320 grit diamond wheel, and their edges were chamfered to minimize fracture initiation at the edges. A total of 26 specimens was prepared; 13 were tested in the as-ground condition (referred to as standard test bars) and the other 13 were mechanochemically polished with  $\text{Fe}_2\text{O}_3$  removing an average of ~26 $\mu\text{m}$  from the ground surface before testing. The samples were fractured in an Instron testing machine using a crosshead speed of ~0.5 mm/mnt. and spacings of 18 mm between the supporting pins and 9 mm between the loading pins.

The results of fracture strength measurements of standard and mechanochemically polished test bars of  $\text{Si}_3\text{N}_4$  are summarized in Table 2. These data were also analyzed using Weibull statistical methods; the results of these analyses are shown in Figures 16 and 17, respectively. It is seen that there is little difference between the strength values of the mechanochemically polished and ground samples of  $\text{Si}_3\text{N}_4$ . In an effort to determine the cause of the observed insensitivity of the fracture strength of hot-pressed  $\text{Si}_3\text{N}_4$  to two significantly different surface finishing treatments, a fractographic analysis of the fractured 4-point-bend specimens will be performed in another program. The results of this analysis will be described elsewhere.

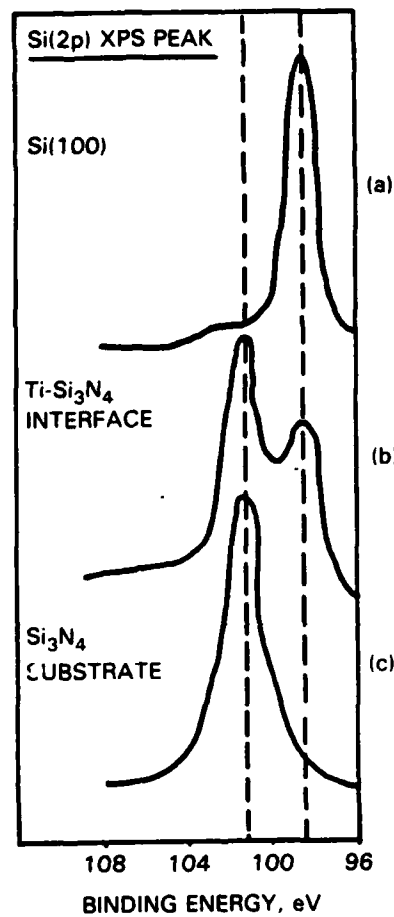


Figure 15.  $\text{Si}_{2p}$  XPS Peak of Si Single Crystal,  $\text{Si}_3\text{N}_4$  and the  $\text{Si}_3\text{N}_4/\text{Ti}$  Interface

Table 2. Fracture Strengths of Standard and Mechanochemically Polished Test Bars of Hot-Pressed  $\text{Si}_3\text{N}_4$

Samples	Mean Fracture Stress MPa (Ksi)	Standard Deviation MPa (Ksi)
Standard	789 (114.5)	113 (16.3)
Mechanochemically polished	768 (111.5)	77 (11.2)

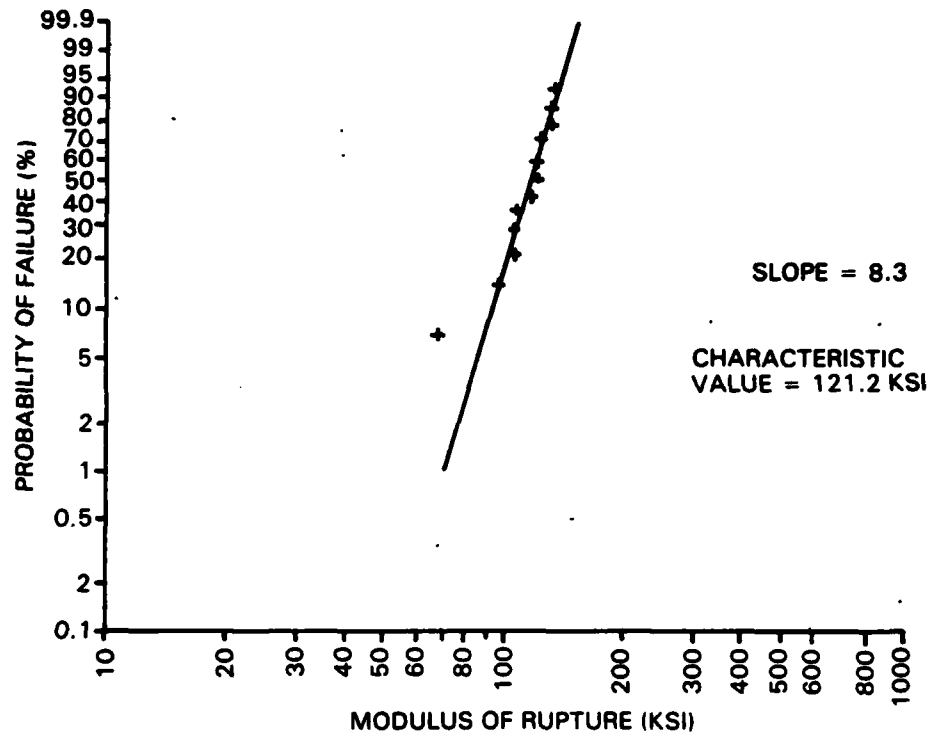


Figure 16. Weibull Plot of Standard Test Bars of Hot-Pressed  $\text{Si}_3\text{N}_4$

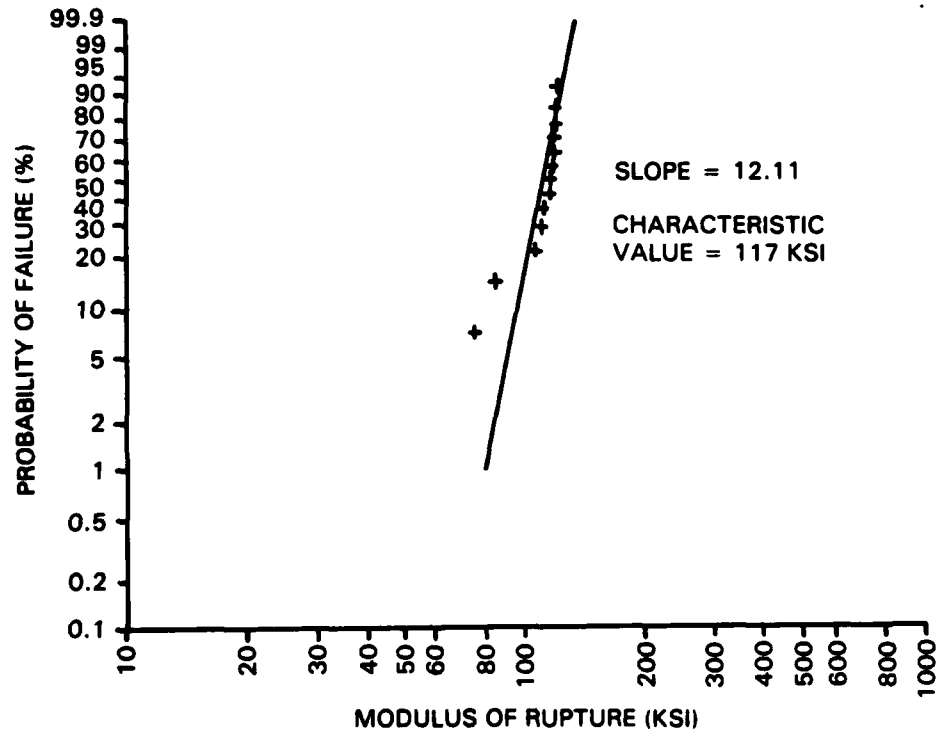


Figure 17. Weibull Plot of Mechanochemically Polished Bars of Hot-Pressed  $\text{Si}_3\text{N}_4$

### 2.3 Other Materials

This section describes the results of our preliminary efforts to develop a mechanochemical polishing technique for GaAs, Spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ),  $\text{ZrO}_2$ , SiC and  $\text{B}_4\text{C}$ .

In the case of GaAs, initial efforts were made to dry mechanochemically polish it with  $\text{CaCO}_3$ ,  $\text{BaCO}_3$  and MgO on a linen bakelite lap. Excessive chipping occurred at the edges of the samples and scratch-free surfaces were not obtained by dry mechanochemical polishing. However, scratch-free and highly reflecting surfaces were obtained when GaAs single crystals were wet mechanochemically polished on a beeswax lap, using a slurry of MgO in water. Optical micrograph and electron channeling pattern of a surface of GaAs crystal wet mechanochemically polished with MgO slurry are shown in Figure 18.

Samples of other materials ( $\text{B}_4\text{C}$ , SiC,  $\text{ZrO}_2$  and spinel) were first lapped with  $15\mu\text{m}$  diamond on a brass lap and then mechanochemically polished on a linen bakelite lap for one hour with  $\text{CaCO}_3$ ,  $\text{BaCO}_3$ , MgO,  $\text{Fe}_2\text{O}_3$ , NiO,  $\text{Sr}_2\text{CO}_3$  and colloidal silica, using a pressure of  $\sim 2 \times 10^4 \text{N/m}^2$  (3 psi). Samples were examined visually and in an optical microscope after mechanochemical polishing. Appearance of highly reflecting or scratch-free areas on the lapped surface was taken as an evidence for mechanochemical polishing. Table 3 lists the abrasives that were found to react mechanochemically with various materials. While these data are preliminary, they are indicative of the broad application of mechanochemical polishing.



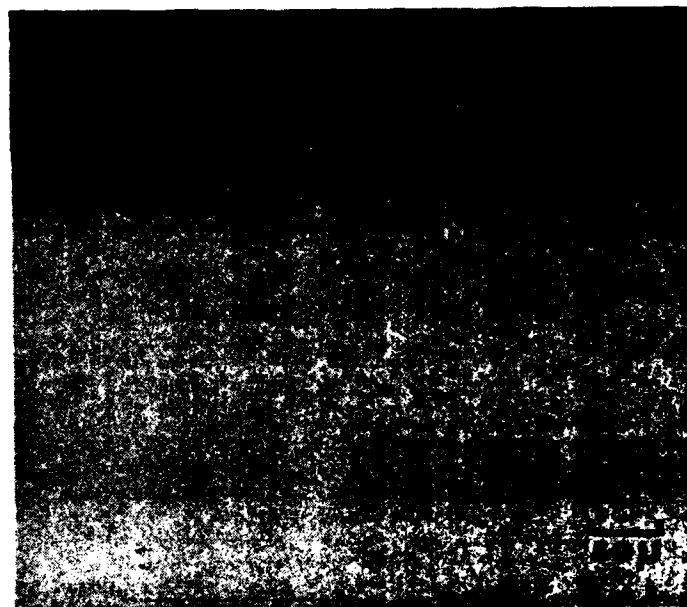


Figure 18. Optical Micrograph and Electron Channeling Pattern of Mechanochemically Polished GaAs

**Table 3. Potential Soft Abrasives for Mechanochemical Polishing of Various Materials**

<b>Material</b>	<b>Abrasives</b>
<b>MgO Al<sub>2</sub>O<sub>3</sub></b>	<b>SrCO<sub>3</sub>, MgO, NiO, Fe<sub>2</sub>O<sub>3</sub>, Colloidal Silica</b>
<b>ZrO<sub>2</sub></b>	<b>MgO, NiO, SrCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Colloidal Silica</b>
<b>SiC</b>	<b>MgO, SrCO<sub>3</sub></b>
<b>B<sub>4</sub>C</b>	<b>SrCO<sub>3</sub>, MgO, NiO, Fe<sub>2</sub>O<sub>3</sub>, Colloidal Silica</b>
<b>GaAs</b>	<b>MgO</b>

### Section 3

#### Discussion

As noted earlier, chemical reactions involved in the surface finishing can broadly be classified into two categories, namely, solid-solid and solid-liquid. Since, in the past, mechanochemical polishing techniques involving solid-liquid types of chemical reactions has been studied in greater detail than that involving solid-solid types of chemical reactions, the emphasis of most of our efforts was on material removal through solid-solid types of chemical reactions, although clear distinction between the two types of reactions was not always made.

The work performed in this program, and the earlier work of Yasunaga et al.<sup>1</sup>, indicates that solid-solid type of chemical reactions are common, can be induced at pressures of the order of a few psi, and can be used for surface finishing. Yasunaga et al. demonstrated mechanochemical polishing for single crystals of silicon, quartz and alumina. In the present work, we have demonstrated the feasibility of mechanochemical polishing of  $\text{Si}_3\text{N}_4$  and identified potential soft abrasives for many more materials, such as  $\text{B}_4\text{C}$ ,  $\text{SiC}$ , and  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  (Table 3).

As compared to mechanochemical polishing of  $\text{Si}_3\text{N}_4$  with  $\text{Fe}_2\text{O}_3$  (Figures 6, 11 and 12) or of Si with  $\text{CaCO}_3$  or  $\text{BaCO}_3$ <sup>1</sup>, the measured removal rates obtained by mechanochemically polishing  $\text{Al}_2\text{O}_3$  with  $\text{SiO}_2$  were much lower, in the range of 0.3-0.6  $\mu\text{m/hr}$  (Figures 3 and 4). The mechanochemical polishing approach pursued in the present work is likely to have a limitation of low removal rate for some more materials.

In addition to high removal rates, high-purity of polished surface and good flatness, there is one more aspect of mechanochemical polishing of  $\text{Si}_3\text{N}_4$  with  $\text{Fe}_2\text{O}_3$  that needs to be emphasized: the lack of orange-peel appearance. Reaction bonded  $\text{Si}_3\text{N}_4$ , and hot-pressed  $\text{Si}_3\text{N}_4$  obtained from three different vendors were polished mechanochemically in the present work. Mechanochemically polished surfaces of none of these  $\text{Si}_3\text{N}_4$  showed any orange-peel appearance. Surfaces of many materials in the polycrystalline form show orange-peel appearance when polished mechanochemically using colloidal silica. In many cases, colloidal silica removes material predominantly through liquid-solid types of chemical reactions at rates which are significantly higher than those achieved by solid-solid type of mechanochemical polishing. For example, sapphire of orientation (1 $\bar{1}$ 02) can be polished at a rate of over 25  $\mu\text{m/hr}$  using colloidal silica.<sup>6</sup>

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<sup>6</sup>H.W. Gutsche and J.W. Moody, J. Elec. Chem. Soc. 125, 136 (1978).

One of the most important motivations for developing mechanochemical polishing technique for a given material is to see if the technique can be used for one-step polishing of that material. For example, from as-ground condition to scratch-free and damage-free condition in one mechanochemical polishing step. This requires high removal rate, whose magnitude varies from material to material. For many hard, polycrystalline ceramics in which the depth of damage introduced by good grinding practices is of the order of a few tens of micrometers, a process that removes material damage free at a rate of a few micrometers per hour could be used for one-step polishing. Much higher removal rates are required for one-step polishing of many semiconductors and glasses in which the grinding or sawing damage extends to a depth of several tens of micrometers.

There are several potential applications for a mechanochemical polishing process that has a limitation of low removal rate. These applications are essentially the ones in which the objective is to improve the performance of a component by removing a small amount of material. One example is the post polishing of a conventionally polished material to remove fine scratches and a thin damaged layer or post polishing of a colloidal silica polished material to remove orange-peel appearance as well as to improve flatness. Another example is the post polishing of diamond-turned optics to remove a defect with record-groove appearance which is frequently observed.

Yet another example is in connection with an observation that is frequently made regarding a contact polishing technique, conventional or mechanochemical. It is the presence of abrasive grains near the polished surface. This may not be acceptable in some cases. For example, the workpiece may be a laser window which is polished with an abrasive A (because it removes material at a high rate) for use in a high-power laser system operating at wavelength  $\lambda$ . If the abrasive A strongly absorbs light of wavelength  $\lambda$ , then its presence near the polished surface will not be acceptable because it would reduce the damage threshold of the window. Assume that the window can be polished mechanochemically with an abrasive B, which removes material at a low rate but does not absorb light of wavelength  $\lambda$ . In such a case, a significant improvement in the damage threshold of the window could be realized by polishing it first with abrasive A, to remove the damage introduced by previous grinding and lapping operations, and then with abrasive B to remove the residue of polishing abrasive A.

## **Index of Publications**

1. K.D. McHenry, R.J. Stokes and B.G. Keopke, "Mechanochemical Polishing of Ceramics," presented at the American Ceramic Society Annual Meeting (1981).
2. J.P. Cummings, L. Weiman, R. Anderson, H. Vora and D. Kompelien, "Processing and Properties of a High Density Chromium/Copper System for Electronics Packaging." Presented at the International Electronics Packaging Conference, Cleveland, Ohio, November 9 and 10, 1981.
3. H. Vora, R.H. Anderson and R.J. Stokes, "Surface Finishing Using Soft Abrasives" in laser induced damage in optical materials: 1981, H.E. Bennett, A.J. Glass, A.H. Guenther and B.E. Newman, editors. To be published as an NBS special publication.
4. H. Vora and R.J. Stokes, "Study of Mechanochemical Machining of Ceramics and the Effect on Thin Flm Behavior," Annual Technical Report #N00014-80-C-0437-1, Contract N00014-80-C-0437, June 1981.
5. H. Vora, T.W. Orent and R.J. Stokes, "Mechanochemical Polishing of Silicon Nitride," J. Am. Ceram. Soc. 65, C-140 (1982).
6. H. Vora and R.J. Stokes, "Study of Mechanochemical Machining of Ceramics and the Effect on Thin Film Behavior," Final Technical Report #N00014-80-C-0437-2, Contract N00014-80-C-0437, January 1983.

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